and ^{1}H spectra were recorded at 25.2 MHz on a Varian XL-100-15 instrument equipped with a Nicolet TT-100 pulsed Fourier transform unit. Typical conditions were 8K data points, 90° pulse, 1.36-s acquisition time, zero delay, 5000–15 0000 acquisitions, 0.2-Hz exponential multiplier, 6000-Hz sweep width, 30 °C. Line widths at half-height were measured on 1000-Hz sweep-width expansions of the original spectra. A line drawn across tops of backbone CH_2 resonances was used as baseline for the CH_2Cl peak.

Swelling of Cross-linked Polymers. A 0.2-g sample of dry polymer was carefully weighed in a fritted-glass tube and soaked at least 2 h in $CHCl_3$ or toluene. The fritted tube was placed in a polyethylene centrifuge tube and centrifuged until all adhering solvent droplets were removed (5–10 min). The sample was reweighed to determine the weight percent of polymer. All experiments were performed at least twice. Estimated errors with $CHCl_3$ are greater than those with toluene because $CHCl_3$ evaporates from the polymer beads at a slow rate even after excess droplets are removed.

Registry No. Styrene, chloromethylstyrene, divinylbenzene copolymer, 55844-94-5; divinylbenzene, styrene copolymer, 9003-70-7.

Excited-State Properties of *cis*- and *trans*-1,2-Di(9-anthryl)ethylenes

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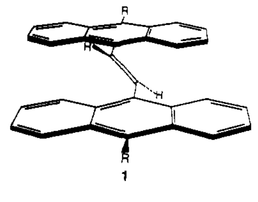
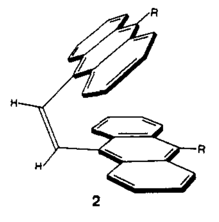
Steric impairment of conjugation in 1,2-diarylethylenes is known to contribute to the different photochemical and photophysical properties which may distinguish geometrical isomers.[1,2] For example, sterically unhindered *trans*-stilbene shows fine structure in its absorption spectrum and, characteristically, its fluorescence spectrum exhibits a small Stokes shift as differences between ground-state and excited-state geometry are small. In *cis*-stilbene, by comparison, the hypsochromically shifted absorption spectrum is less intense and less structured due to steric interaction of the aromatic hydrogens in the ortho positions. Moreover, because of the reduced lifetime in its excited singlet state, *cis*-stilbene in solution at room temperature is nonfluorescent. At 77 K in rigid media, however, the fluorescence quantum yield of *cis*-stilbene is as high as 0.75.

We report here on the excited state properties of *trans*- and *cis*-1,2-di(9-anthryl)ethylenes 1 and 2. Their respective geometries are intriguing inasmuch as neither one of the two geometrical isomers can assume a ground-state conformation in which the two anthracene systems are coplanar with the central ethylene bond. Inspection of Dreiding molecular models suggests that *trans*-1,2-di(9-anthryl)ethylenes 1 may alleviate intramolecular hydrogen interaction by deviation from planarity brought about by twists of about 50° around the two aryl–ethylene single bonds. In the resulting conformer, the two anthracene systems are alligned parallel as shown in 1. Steric relief can also be achieved by twists around the single bonds in mutally opposite directions so as to give a conformer in which the planes of the two anthracene systems would be in perpendicular arrangement. Accordingly, the electronic absorption spectra of *trans*-1,2-di(9-anthryl)ethylenes show little fine structure and only small bathochromic shifts relative to the absorption spectra of the correspondingly substituted 1,2-di(9-anthryl)ethanes, and in comparison to those of di(9-anthryl)acetylenes (see Figure 1).[3-5]



1

a: R = H
b: R = $OCOCH_3$
c: R = OCH_3



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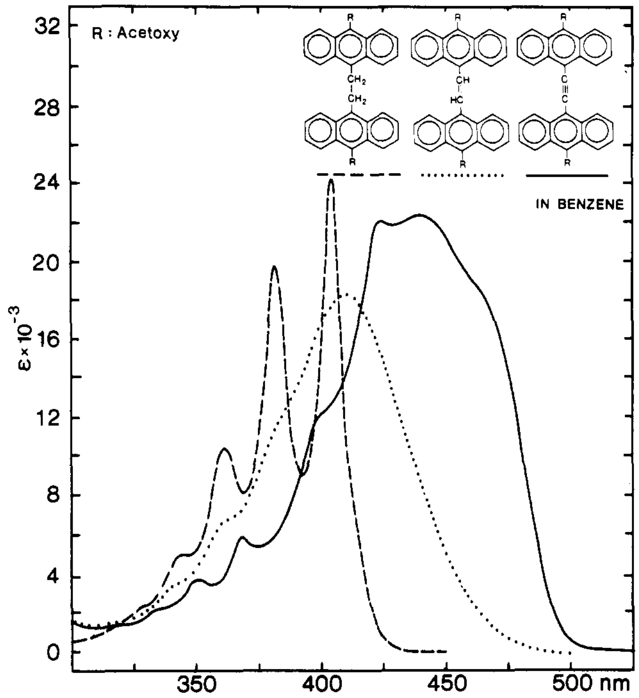

Figure 1. Electronic absorption spectra of 1,2-bis(10-acetoxy-9-anthryl)ethane (dashed curve), *trans*-1,2-bis(10-acetoxy-9-anthryl)ethylene (dotted curve), and bis(10-acetoxy-9-anthryl)acetylene (solid curve) in benzene solution.

cis-1,2-Di(9-anthryl)ethylenes 2, apparently, have not been described heretofore.[6] Stereochemical considerations suggest that the planes of their two anthracene systems on one hand and the plane of the ethylene bond on the other hand may be in a mutually perpendicular arrangement. Consequently, the two anthracene moieties would face each other in relatively rigid geometry.

Using conventional fluorescence spectrometry, we find that *trans*-1,2-di(9-anthryl)ethylene (**1a**),[7] contrary to an earlier report,[8] actually is fluorescent in solutions at room temperature. Likewise, substituted[4] *trans*-1,2-di(9-anthryl)ethylenes **1b** and **1c** are found to be luminescent in solution at room temperature. Remarkably, in every case the broad, structureless luminescence is characterized by a gap of about 10 000 cm^{-1} between absorption and

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[1] (a) Fischer, G.; Seger, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1569. (b) Goedicke, Ch.; Stegemeyer, H.; Fischer, G.; Fischer, E. *Z. Phys. Chem. N. F.* **1976**, *101*, 181. (c) Fischer, E. *J. Phys. Chem.* **1980**, *84*, 403. (d) Sharafy, Sh.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4119.

[2] Turro, N. J. "Modern Molecular Photochemistry"; The Benjamin/Cummings Publishing Company, Inc.: Menlo Park, CA, 1978; p 113.

[3] Becker, H.-D.; Sanchez, D. *Tetrahedron Lett.* **1975**, 3745.

[4] Becker, H.-D.; Sanchez, D.; Arvidsson, A. *J. Org. Chem.* **1979**, *44*, 4247.

[5] Akiyama, S.; Nakasuji, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1972**, *44*, 2231.

[6] The physical properties of a compound believed to be **2a** (see ref 8) were recently found to be those of 9-cyanoanthracene (cf. ref 4).

[7] Horner, L.; Beck, P.; Toscano, G. *Chem. Ber.* **1961**, *94*, 1323.

[8] Nagornaya, L. L.; Nurmukhametov, R. N.; Malkes, L. Y.; Shubina, L. V. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1963**, *27*, 748.

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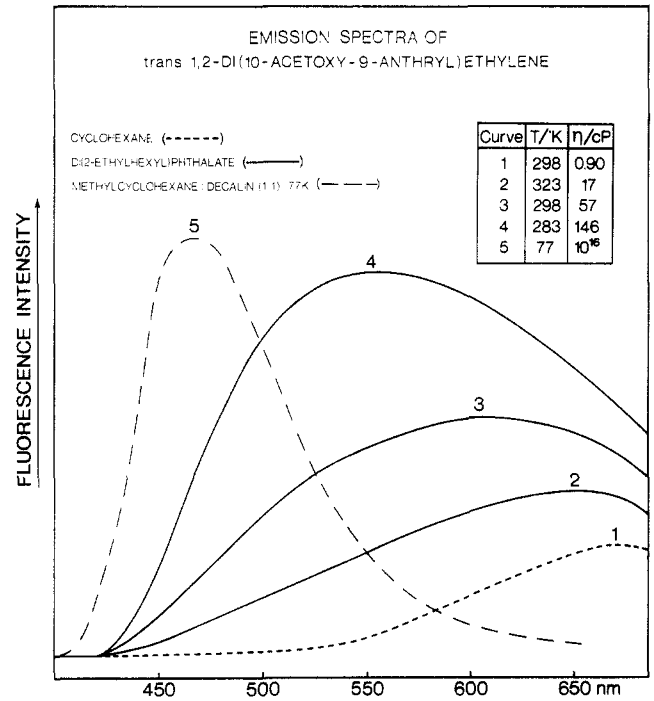
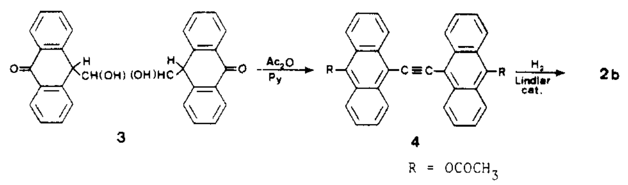


Figure 2. Emission spectra of *trans*-1,2-bis(10-acetoxy-9-anthryl)ethylene at varying viscosity in cyclohexane (curve 1), bis(2-ethylhexyl) phthalate (curves 2–4), and methylcyclohexane/decalin (1:1) glass (curve 5).

emission maxima. For example, *trans*-1,2-bis(10-acetoxy-9-anthryl)ethylene (**1b**) in cyclohexane solution (λ_{max}^{abs} 407 nm) exhibits its fluorescence maximum at 670 nm, suggesting very large conformational differences between ground state and excited state. The fluorescence quantum yield at room temperature is 2×10^{-3} and, in accordance with the obvious differences between the geometry of the ground state and that of the emitting excited state of **1b**, both the quantum yield of fluorescence and the emission energy increase with increasing solvent viscosity (cf. ref 1). In a glassy matrix (decalin/methylcyclohexane, 1:1)[9] at 77 K, the emission maximum is shifted to 465 nm (see Figure 2), and the emission quantum yield was found to be 0.8.

Attempts to photochemically convert *trans*-1,2-di(9-anthryl)ethylenes **1** into their cis isomers **2** were not successful. However, the unambiguous synthesis of *cis*-1,2-bis(10-acetoxy-9-anthryl)ethylene (**2b**) was accomplished in a straightforward manner by catalytic hydrogenation of bis(10-acetoxy-9-anthryl)acetylene (**4**) which, in turn, was prepared from the known[10] dianthronyl glycol **3** by treatment with acetic anhydride in pyridine solution.



The electronic absorption spectrum of *cis*-1,2-bis(10-acetoxy-9-anthryl)ethylene (**2b**), in comparison to that of its trans isomer **1b**, is characterized by a hypsochromic shift and, significantly, by the exhibition of the fine structure pattern typical of the anthracene chromophore

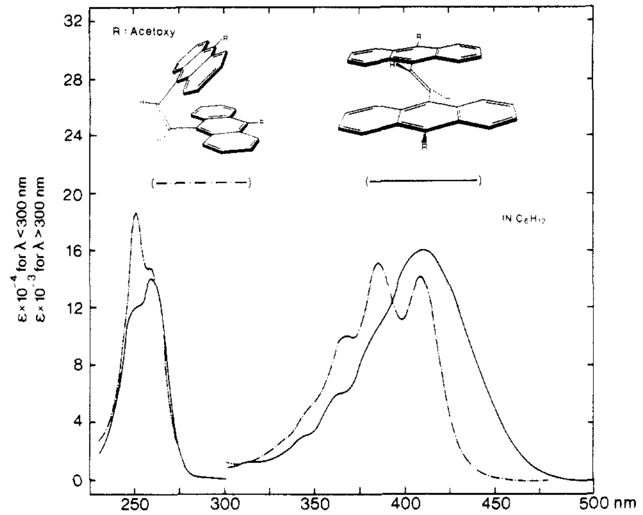
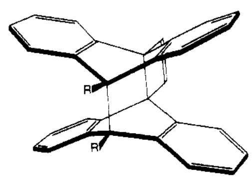


Figure 3. Electronic absorption spectra of *cis*-1,2-bis(10-acetoxy-9-anthryl)ethylene (broken curve) and *trans*-1,2-bis(10-acetoxy-9-anthryl)ethylene (solid curve) in cyclohexane solution.

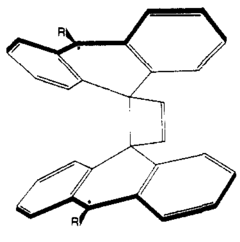
(see Figure 3). Both features are in accord with the electronic consequences of the molecular geometry discussed above for *cis*-1,2-di(9-anthryl)ethylenes.

Concerning its excited-state properties, *cis*-di(9-anthryl)ethylene **2b** in cyclohexane solution at room temperature is virtually nonfluorescent ($\Phi_F < 10^{-4}$). In rigid medium (decalin/methylcyclohexane, 1:1) at 77 K, **2b** gives rise to weakly structured emission (λ_{max}^{em} 460 nm; Φ_F 0.2) which extends noticeably into the low-energy region of the visible spectrum. Similarly, crystalline **2b** at room temperature shows (structureless) emission (λ_{max}^{em} 485 nm) extending beyond 600 nm. Conceivably, excimer-like intramolecular interactions of the two anthracene moieties in **2b** are responsible for the broadness of emission.

Interestingly, the quantum yield of photochemical isomerization of *cis*-1,2-di(9-anthryl)ethylene **2b** into its trans isomer **1b** was found to be as low as 9×10^{-3} (at room temperature in cyclohexane solution). Furthermore, we have found no evidence for a seemingly feasible intramolecular $[4_\pi + 4_\pi]$ cycloaddition to give **5**. Apparently,



5



6

photo excited *cis*-1,2-di(9-anthryl)ethylene **2b** most efficiently returns to ground state by radiationless transition. Reversible formation of biradical species such as **6**, analogous to intermediates discussed in the photochemistry of dianthrylethanes,[11] may be responsible for the inefficient photochemistry of *cis*-1,2-di(9-anthryl)ethylenes.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark. ^{1}H NMR spectra were recorded on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Ab-

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[9] Greenspan, H.; Fischer, E. *J. Phys. Chem.* **1965**, *69*, 2466.

[10] Fairweather, D. A. W.; McGechen, J. F. U.S. Patent 2842561 (to ICI Ltd.), July 8, 1958; *Chem. Abstr.* **1959**, *53*, 9682.

[11] Bergmark, W. R.; Jones, G., II; Reinhardt, T. E.; Halpern, A. M. *J. Am. Chem. Soc.* **1978**, *100*, 6665.

sorption and emission spectra were obtained on a Beckman Acta III spectrophotometer and an Aminco SPF 500 (corrected spectra) spectrofluorometer, respectively.

***cis*-1,2-Bis(10-acetoxy-9-anthryl)ethylene (2b).** A solution of bis(10-acetoxy-9-anthryl)acetylene (40 mg) in ethyl acetate (200 mL) was hydrogenated under normal conditions over Lindlar catalyst (580 mg). After uptake of 1 molar equiv of hydrogen (1 h), the catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The residue was recrystallized from methylene chloride by addition of cyclohexane to give pale yellow crystals (26 mg, 65%): mp 248–252 °C; ^{1}H NMR (acetone-d_6) δ 8.3 (d, 4 arom H, J = 9 Hz), 8.1 (s, 2 H, ethylene H), 7.8 (d, 4 arom H, J = 9 Hz), 7.3 (m, 8 arom H), 7.1 (m, 8 arom H), 2.5 (s, 6 H, acetoxy group). The doublets are slightly broadened due to meta coupling. Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.24; H, 4.87. Found: C, 82.02; H, 4.96.

In the ^{1}H NMR spectrum of the trans isomer **1b** in acetone-d_6, the ethylenic protons give rise to a singlet at δ 7.85, and the acetoxy groups give rise to a singlet at δ 2.7. The signals due to the aromatic protons in **1b** appear as three multiplets centered at δ 7.6, 8.15, and 8.7, respectively.

Bis(10-acetoxy-9-anthryl)acetylene (4). A stirred suspension of 1,2-di(10-anthronyl)-1,2-dihydroxyethane (**3**;[10] 2.68 g) in a mixture of pyridine (50 mL) and acetic anhydride (20 mL) was kept at 47 °C for 24 h to give a clear red-brown solution. The reaction mixture was poured into methanol (150 mL) whereupon a red-brown crystalline precipitate formed. The precipitate (1.83 g) consists of a mixture of the acetylene **4** and the previously known (cf. ref 4) dianthronylidenethane (approximate ratio 1:1). Separation of the two products was accomplished by column chromatography (SiO_2/CH_2Cl_2). The yield of **4** (orange-red crystals of low solubility, mp 289–295 °C) was 30% based on **3**: ^{1}H NMR ($CDCl_3$) δ 8.9 (d, 4 H, J = 8 Hz), 8.05 (d, 4 H, J = 8 Hz), 7.6 (m, 8 H) [meta coupling (J = 1 Hz) detectable for all four types of aromatic protons], 2.69 (s, 6 H, acetoxy group). Anal. Calcd for $C_{34}H_{22}O_4$: C, 82.58; H, 4.48. Found: C, 82.33; H, 4.46.

Photochemical Experiments. Quantum yields of emission are based on the fluorescence quantum yield of 9,10-diphenylanthracene (Φ = 0.83).[12] The photochemical isomerization of **2b** into **1b** was brought about by irradiating a 3 × 10^{-4} M solution in cyclohexane, using light of 366-nm wavelength. The formation of **1b** was monitored by measuring the increase of absorption at 450 nm in conjunction with the decrease of the **2b** absorption around 370 nm. For the determination of the quantum yield of isomerization, the intramolecular photochemical cycloadditon of 1,2-di(9-anthryl)ethane (Φ = 0.26)[13] was used in the actinometric experiment.

Acknowledgment. We are indebted to Professor Ernst Fischer, Rehovot, Israel, for a stimulating discussion and for helpful comments regarding the manuscript.

Registry No. 1b, 75919-24-3; **2b**, 75919-25-4; **3**, 75919-26-5; **4**, 75919-27-6; 1,2-bis(10-acetoxy-9-anthryl)ethane, 58382-04-0.

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[12] Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; p 317.

[13] Livingston, R.; Wei, K. S. *J. Am. Chem. Soc.* **1967**, *89*, 3098.

Unsaturated Carbenes. 14. Divinyl Sulfides via Insertion of Isopropylidenecarbene into Enethiols[1]

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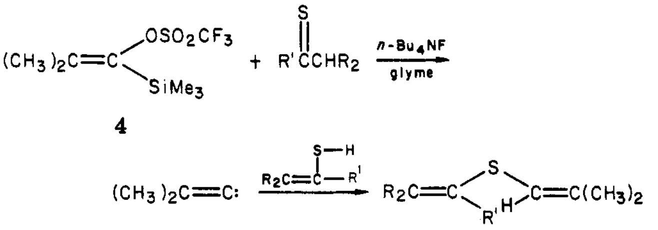
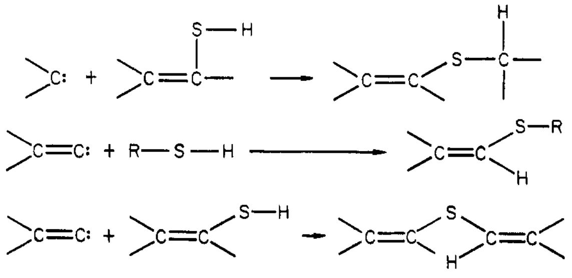
Carbene insertions into X–H bonds such as C–H, Si–H, O–H, and others are well-known and in many instances result in synthetically useful products.[2] Similarly, unsaturated carbenes readily insert into Si–H, O–H, and N–H bonds.[3] Little is known, however, about the insertion of either species into S–H bonds and in particular the S–H of enethiols.[4] Insertion of carbenes into enethiols or of unsaturated carbenes into alkyl thiols would result in alkyl vinyl sulfides, whereas interaction of unsaturated carbenes with enethiols should give divinyl sulfides. Although dialkyl and alkyl vinyl sulfides are well-established compounds, little is known about divinyl sulfides.[5] Hence in this note we report the formation of divinyl sulfides by the interaction of isopropylidenecarbene with several thiones.

Scheme I





Dialkyl thiones **1–3** were prepared from the corresponding commercially available carbonyls by standard procedures.[6] As these thiones react with strong bases, such as *t*-BuOK, the carbene was generated[7] from silylvinyl triflate **4** with tetrabutylammonium fluoride as shown in Scheme I.

Interaction of the thione, dissolved in glyme at −23 °C, with a 10% molar excess of triflate **4** gave, upon addition of R_4NF, divinyl sulfides **5–7** in 25–40% yield. The products were isolated by medium-pressure LC and characterized by spectral means as summarized in Table I. The spectral data are in complete accord with the proposed structures.

It is well-known that the ene thiol content of these dialkyl thiones is in the 20–40% range.[6] Furthermore, unlike carbonyls, the thione ⇄ enethiol tautomerization is believed to be very slow, with separation and isolation of the individual tautomers possible.[6] Since we made no attempt to separate the tautomers, the formation of divinyl sulfides **5–7** may actually be quantitative, based on the enethiols consumed. In conclusion, interaction of unsaturated carbenes with thiocarbonyls provides a simple, general means of preparing pure divinyl sulfides, albeit in only modest isolated yields.

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[1] Paper 13: Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6813.

[2] Hine, J. "Divalent Carbon"; Ronald Press: New York, 1964. Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. Jones, M., Jr.; Moss, R. A. "Carbenes"; Wiley-Interscience: New York, 1973, Vol. 1; 1975, Vol. 2.

[3] Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

[4] We are not aware of the interaction of *any* free carbenes with thiocarbonyls. The addition of diazoalkanes to thiones has been extensively investigated: Beiner, J. A. et al. *Bull. Soc. Chim. Fr.* **1973**, 1979–1983; Pagner, D.; Vialle, J. *Ibid.* **1969**, 3327; Clinet, J.-C.; Julia, S. *J. Chem. Res. (M)* **1978**, 1714–1726.

[5] Stirling, C. J. M., Ed. "Organic Sulphur Chemistry"; Butterworths: London, 1975.

[6] Pagner, D.; Vialle, J. *Bull. Soc. Chim. Fr.* **1969**, 3595.

[7] Stang, P. J.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1667.

0022-3263/81/1946-0823$01.00/0